JP-A 2003-204299

[Document Name] Patent Application
[Applicant's Reference Number] OSK-5141
[Filing Date] July 31, 2003
[To] Commissioner, Patent Office
[IPC] H01G 9/00
[Inventor]
[Address or Residence] 5-5-32-B506, Torikainishi, Settsu-shi, Osaka, Japan
[Name] Mutsuaki MURAKAMI
[Address or Residence] 1-10-6-412, Kamihamuro, Takatsuki-shi, Osaka, Japan
[Name] Hiroyuki FURUTANI
[Applicant]
[Identification Number] 000000941
[Name] KANEKA CORPORATION
[Representative] Masatoshi TAKEDA
[Indication of Fee]
[Number of Deposit Ledger] 005027
[Amount of Payment] 21000 yen
[List of Attached Documents]
[Document Name] Specification 1
[Document Name] Drawings 1
[Document Name] Abstract 1
[Request of Proof] Yes

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[Document Name] Description

[Title of the Invention] ELECTROLYTE AND CAPACITOR USING THE ELECTROLYTE

[Scope of Claims for Patent]

[Claim 1] An electrolyte comprising

at least both an ionic liquid and a conductive polymer as essential ingredients.

[Claim 2] The electrolyte according to Claim 1, wherein

the ionic liquid is a halogen-free ionic liquid.

[Claim 3] An electrolyte to be used for an electrolytic capacitor, comprising

at least both an ionic liquid and a conductive polymer as essential ingredients.

[Claim 4] The electrolyte according to Claim 3, wherein

the ionic liquid is a halogen-free ionic liquid.

[Claim 5] The electrolyte according to Claim 3 or 4, wherein

an anionic component of the ionic liquid comprises a carboxylate ion ($-COO^-$).

[Claim 6] The electrolyte according to Claim 3 or 4, wherein

an anionic component of the ionic liquid comprises a sulfonic acid anion ($-SO_3^-$).

[Claim 7] The electrolyte according to any one of Claims 1 to 6, wherein

the conductive polymer is at least one selected from polypyrrole, polyaniline, polythiophene, and derivatives thereof.

[Claim 8] The electrolyte according to any one of Claims 1 to 7, wherein

the ionic liquid is added with at least one salt selected from ammonium salts, amine salts, quaternary ammonium salts, and organic acids.

[Claim 9] A capacitor comprising the electrolyte according to any one of Claims 1 to 8.

[Detailed Description of the Invention]

[0001]

[Technical Field of the Invention]

The present invention relates to an electrolyte having electron conductivity and ion conductivity. More specifically, the present invention relates to an electrolyte to be used for an electrolytic capacitor.

[0002]

[Background Art]

An electrolytic capacitor generally includes an anode composed of a valve metal such as aluminum or tantalum, a dielectric composed of an oxide film formed on the surface of the anode, and a cathode formed to hold an electrolyte between the cathode and the dielectric. In the electrolytic capacitor, the driving electrolyte has two important functions. One of the two is the function called anodization to protect and repair a very thin oxide film. The other is the function as the actual cathode, namely, a function to extract a capacitance from the dielectric formed on the anode.

[0003]

The first function, i.e., anodization, is a chemical reaction to form an aluminum or tantalum oxide film on the basis of the ion conductivity possessed by the electrolyte. Although it has been known that protons play an important role in anodization, the ions involved in the anodization have not been clearly defined. Therefore, currently the electrolyte having anodizing property is searched by a trial and error basis.

[0004]

On the other hand, the another function as the actual cathode is required to have high electric conductivity, i.e., high electron conductivity.

[0005]

As the electrolyte of the electrolytic capacitor, an organic solvent such as ethylene glycol or γ-butyrolactone containing an organic acid, an inorganic acid, or a salt thereof

is generally used. Specific examples of the organic acid, the inorganic acid, or the salt thereof include phosphoric acid, formic acid, acetic acid, ammonium adipate, ammonium succinate, tertiary amines, and quaternary ammonium salts. Such a composite electrolytic system using the liquid electrolyte containing an electrolytic substance and a solvent is used for forming an electrolyte having both of the aforementioned ion conductivity and electron conductivity (see Non-Patent Documents 1, 2, 3, and 4).

Although the conductivity of such a liquid electrolyte is improved by adding the above-described additive, the conductivity is only about 10^{-3} S/cm, which is unsatisfactory for realizing a low-impedance capacitor. Also, the liquid electrolyte causes a dry-up phenomenon due to evaporation of the solvent used, and thus the electrolyte is unsatisfactory in the long-term life and heat resistance.

[0006]

In order to improve these properties, use of a molten salt as an electrolyte for a capacitor has been investigated. For example, an investigation has been conducted for forming an electrolyte for a capacitor by melting or melting and then solidifying an electrolytic salt having a nitrogen-containing heterocyclic cation containing a conjugated double bond or a nitrogen-containing heterocyclic ring containing a conjugated double bond without using a solvent (see, for example, Patent Document 1).

[0007]

Also, an investigation has been conducted for forming a capacitor including an electrolyte for an electrolytic capacitor interposed singly or together with a separator between an anode foil and a cathode, the electrolyte being prepared by melting a mixture of a carboxylate and a carboxylic acid without using a solvent (see, for example, Patent Document 2). However, these electrolytes are insufficient in terms of the conductivity or the cost, and therefore the electrolytes

have not yet been put into practical applications.

[0008]

On the other hand, solid type capacitors not containing a solvent have been recently developed. Specifically, these capacitors each include, as an electrolyte, a conductive polymer such as polypyrrole, polyaniline, or a polythiophene derivative. Since these conductive polymers have extremely higher electric conductivity (electron conductivity) than the above-described conventional liquid electrolytes each containing an electrolytic substance and a solvent, the internal impedance of a capacitor using such a conductive polymer as an electrolyte can be decreased. In particular, when these conductive polymer capacitors are used for high-frequency circuits, excellent properties are exhibited. Therefore, such conductive polymer capacitors are establishing an important position in the electrolytic capacitor market.

[0009]

However, conductive polymers basically do not have ion conductivity, and thus conductive polymer capacitors are far inferior to conventional capacitors each including a liquid electrolyte in the anodizing function to repair oxide films of electrolytic capacitors. It is generally said that in a conductive polymer capacitor, due to the Joule heat generated in damage to a dielectric film, a conductive polymer present on a damaged portion of the dielectric surface is insulated by the de-doping reaction of the conductive polymer, thereby preventing the breakage of the dielectric film. Such a mechanism is fundamentally different in principle from the mechanism occurring in the function to repair an oxide film of a conventional capacitor using a liquid electrolyte (see, for example, Non-patent Document 5).

[0010]

Consequently, the conductive polymer capacitors are disadvantageous in that capacitors with a high withstand voltage cannot be provided. Specifically, under present

conditions, when aluminum is used for an anode, a conductive polymer capacitor having a withstand voltage up to only about 16 V can be produced, for example, with a formation voltage of 70 V, and when tantalum is used, a conductive polymer capacitor having a withstand voltage up to only about 12 V can be produced, for example, with a formation voltage of 34 V. The terms "formation voltage of 70 V" mean that in forming a dielectric oxide film on a valve metal surface, the DC voltage applied to the valve metal, i.e., the formation voltage, is 70 V. Of course, the withstand voltage can be basically increased by increasing the formation voltage. In this case, however, the capacitance of a capacitor decreases as the formation voltage increases, and thereby the properties of a capacitor deteriorate. Also, the withstand voltage does not increase in proportion to increases in the formation voltage. Therefore, this method may not be said to be a preferred method.

[0011]

Apart from the above-described technique relating to electrolytic capacitors, molten salts in a liquid state at room temperature have been recently developed and attracted attention. The molten salt, referred to as an "ionic liquid", includes a combination of a quaternary salt cation, such as imidazolium or pyridinium, with an appropriate anion (e.g. Br^-, $AlCl^-$, BF_4^-, or PF_6^-), and mostly contains a halogen. The ionic liquid has the properties such as nonvolatility, noninflammability, chemical stability, high ion conductivity, and the like, and attracts attention as a reusable green solvent used for various syntheses and chemical reactions such as catalytic reaction. On the other hand, application of the ionic liquid as an electrolyte for a lithium ion battery or as an electrolyte for an electric double layer capacitor has been examined (see, for example, Patent Documents 3 to 10). For example, Non-Patent Document 6 comprehensively discloses a method for synthesizing an ionic liquid. However, there has been no example of investigation of the ionic liquid from the

viewpoint of the function to repair an oxide film, i.e., anodizing property.

[0012]

There have been cases of studies for synthesizing a conductive polymer in an ionic liquid. Some of those cases have reported the electrolytic polymerization of a conductive polymer such as polypyrrole or polythiophene in an ionic liquid in which an anion is $AlCl_4^-$ (see, for example, Non-Patent Documents 7, 8, and 9). In such cases, $AlCl_4^-$ which is the anion of the ionic liquid is used also as a dopant for the conductive polymer to be formed by the electrolytic polymerization. However, due to the presence of the $AlCl_4^-$ which is unstable in the air, the resulting conductive polymer has extremely unstable electric conductivity. Further, although the anion is taken in the conductive polymer in those cases, the ionic liquid itself is not taken in the electrolytic polymer. Moreover, there are cases where electrolytic polymerization of pyrrole or aniline is performed in an ionic liquid in which the anion used is BF4- or PF6- (see, for example, Non-Patent Documents 10 and 11). In all of the foregoing cases, however, the ionic liquids are used simply as solvents for the electrolytic polymerization of the conductive polymers, and the ionic liquids are not taken in the conductive polymers. Additionally, all of the ionic liquids used are halogen-containing ionic liquids.

[0013]

Patent Document 1: Japanese Unexamined Patent Application Publication No. H05-13278

[0014]

Patent Document 2: Japanese Unexamined Patent Application Publication No. H05-101983

[0015]

Patent Document 3: Japanese Unexamined Patent Application Publication No. 2000-3620

[0016]

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Patent Document 4: Japanese Unexamined Patent Application Publication No. H10-83821

[0017]

Patent Document 5: Japanese Unexamined Patent Application Publication No. H11-100347

[0018]

Patent Document 6: Japanese Unexamined Patent Application Publication No. 2002-3478

[0019]

Patent Document 7: WO 00/57440

[0020]

Patent Document 8: Japanese Unexamined Patent Application Publication No. 2002-151361

[0021]

Patent Document 9: Japanese Unexamined Patent Application Publication No. H10-168028

[0022]

Non-Patent Document 1: Denkai Chikudenki Hyoron (Electrolytic Condenser Review), Vol. 28, No. 1, p. 1(1974)

[0023]

Non-Patent Document 2: Denkai Chikudenki Hyoron (Electrolytic Condenser Review), Vol. 47, No. 2, p. 100(1997)

[0024]

Non-patent Document 3: Denkai Chikudenki Hyoron (Electrolytic Condenser Review), Vol. 53, No. 1, p. 101(2002)

[0025]

Non-Patent Document 4: Denkai Chikudenki Hyoron (Electrolytic Condenser Review), Vol. 46, No. 1, p. 123(1995)

[0026]

Non-patent Document 5: Denkai Chikudenki Hyoron (Electrolytic Condenser Review), Vol. 53, No. 1, p. 95(2002)

[0027]

Non-Patent Document 6: "Ionic Liquid", Hiroyuki Ono, CMC Publishing Co., Ltd(2003)

[0028]

Non-Patent Document 7: P. G. Pickup and R. A. Osteryoung, J. Am. Chem., Soc, 106, 2294(1984)

[0029]

Non-Patent Document 8: P. G. Pickup and R. A. Osteryoung, J. Electroanal. Chem., 195, 271(1985)

[0030]

Non-Patent Document 9: L. Janiszewska. And R. A. Osteryoung, J. Electrochem. Soc., 134, 2787(1987)

[0031]

Non-Patent Document 10: W. Lu. et al., Science, 297, 983(2002)

[0032]

Non-Patent Document 11: K. Sekiguchi, M. Atobe and T. Fuchigami, Electrochem. Commun., 4, 881(2002)

[0033]

[Problems to be solved by the Invention]

Considering the above-described situation, the present invention aims to provide an electrolyte which has excellent electron conductivity and excellent ion conductivity. The present invention also aims to provide an electrolyte which, when produced as an electrolyte for a capacitor, makes it possible to provide an electrolytic capacitor having low impedance and high withstand voltage derived respectively from the excellent electron conductivity and the excellent anodizing property of the electrolyte.

[0034]

[Means for Solving the Problems]

(1) The first aspect of the present invention is an electrolyte containing at least both an ionic liquid and a conductive polymer as essential ingredients.

(2) The second aspect of the present invention is the electrolyte described in the above (1), wherein the ionic liquid is a halogen-free ionic liquid.

(3) The third aspect of the present invention is an electrolyte to be used for an electrolytic capacitor,

containing at least both an ionic liquid and a conductive polymer as essential ingredients.

(4) The fourth aspect of the present invention is the electrolyte described in the above (3), wherein the ionic liquid is a halogen-free ionic liquid.

(5) The fifth aspect of the present invention is the electrolyte described in the above (3) or (4), wherein an anionic component of the ionic liquid comprises a carboxylate ion.

(6) The sixth aspect of the present invention is the electrolyte described in the above (3) or (4), wherein an anionic component of the ionic liquid comprises a sulfonic acid anion ($-SO_3^-$).

(7) The seventh aspect of the present invention is the electrolyte described in any one of the above (1) to (6), wherein the conductive polymer is at least one selected from polypyrrole, polyaniline, polythiophene, and derivatives thereof.

(8) The eighth aspect of the present invention is the electrolyte described in any one of the above (1) to (7), wherein the ionic liquid is added with at least one salt selected from ammonium salts, amine salts, quaternary ammonium salts, and organic acids.

(9) The ninth aspect of the present invention is a capacitor including the electrolyte described in any one of the above (1) to (8).

[0035]

[Modes for Carrying Out the Invention]

As a result of various investigations for resolving the above-described problems, the inventors of the present invention have found that some of a series of compound groups referred to as "ionic liquids" exhibit an excellent anodizing property, resulting in the achievement of the present invention. Briefly, it is possible to provide an electrolyte which is excellent in both electron conductivity and ion conductivity by compounding the ionic liquid with anodizing property

according to the present invention and a conductive polymer. The electrolyte is suitably used for a capacitor.

[0036]

An ionic liquid is referred to also as a "room-temperature molten salt" and is liquid at room temperature in spite of being composed only of ions. Unlike ordinary organic solvents which are partially ionized or dissociated, the ionic liquid is composed only of ions. In other words, it is thought that the ionic liquid is 100% ionized. Although the terms "ionic liquid" generally mean an ionic liquid that is liquid at room temperature, the ionic liquid used in the present invention is not necessarily liquid at room temperature as long as it becomes liquid upon aging or heat treatment of a capacitor to spread over the whole of an electrolyte of the capacitor and becomes liquid by the Joule heat generated during repair of an oxide film.

[0037]

The present inventors have synthesized various kinds of ionic liquids and examined the anodizing property of those ionic liquids. In general, an ionic liquid comprises a combination of a cation such as imidazolium and an appropriate anion (such as Br^-, $AlCl^-$, BF_4^-, and PF_6^-), in which a halogen is contained in many cases. However, some ionic liquids are composed of a series of ingredients in which a halogen is not contained.

[0038]

The inventors of the present invention have found that some of the halogen-free ionic liquids have a certain degree of anodizing ability, while no anodizing ability is observed in the ionic liquids in which the anion is $AlCl^-$, Cl^-, Br^- or the like. As described later, the anodizing ability was estimated by applying a voltage to an aluminum plate with a purity of 99.9% that was immersed in the ionic liquid and measuring changes in the electric current intensity.

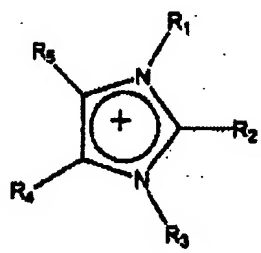
[0039]

Examples of the cation to be used for the ionic liquids

that are suitable for the object of the present invention include imidazolium cations (Formula 1), pyridinium cations (Formula 2), pyrrolidinium cations (Formula 3), ammonium cations (Formula 4), and triazine derivative cations (Formula 5).

[0040]

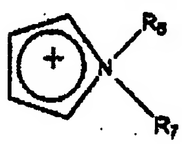
[Chem. 1]



(Formula 1)

[0041]

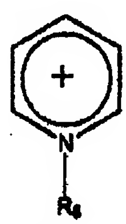
[Chem. 2]



(Formula 2)

[0042]

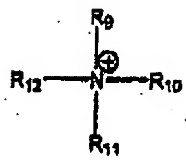
[Chem. 3]



(Formula 3)

[0043]

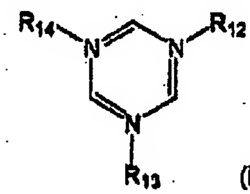
[Chem. 4]



(Formula 4)

[0044]

[Chem. 5]



(Formula 5)

In the above Formulas 1 to 5, each of R_1 to R_{11} represents H, an alkyl group, a vinyl group or an alkoxy group.

[0045]

Examples of the anion include NO_3^-, $RCOO^-$, RSO_3^-, $NH_2CHRCOO^-$, and SO_4^{2-} (in which R represents an alkyl group). Ionic liquids using anions that contain a carboxylate ion ($-COO^-$), such as $RCOO^-$, $^-OOCRCOOH$, $^-OOCRCOO^-$, and $NH_2CHRCOO^-$, are preferably used in the present invention among the above examples. Specifically, it is advantageous to synthesize ionic liquids by using formic acid, acetic acid, maleic acid, adipic acid, oxalic acid, phthalic acid, succinic acid, an amino acid and the like.

[0046]

Moreover, ionic liquids using anions that contain a sulfonic acid anion ($-SO_3^-$) are preferably used for the object of the present invention. Specifically, it is advantageous to synthesize ionic liquids by using benzenesulfonic acid, toluenesulfonic acid, alkylbenzenesulfonic acid, naphthalenesulfonic acid, alkylnaphthalenesulfonic acid, anthraquinonesulfonic acid, polyvinylsulfonic acid, m-sulfonic acid, alkylsulfonic acid, and the like. Among the above, p-toluenesulfonic acid is more preferably used for the

object of the present invention considering that various kinds of ionic liquids can be synthesized using p-toluenesulfonic acid.

[0047]

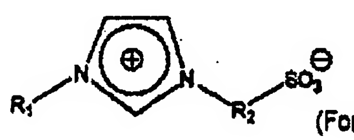
The ionic liquid of the present invention includes a combination of the anion and the cation described above and can be synthesized by a known method. Specifically, a method such as an anion exchange method, an acid ester method, or a neutralization method can be used, and these synthesis methods are described in Non-Patent Document 6.

[0048]

Zwitterion-type ionic liquids each containing a cation and an anion bonded together by a covalent bond may be preferably used for the object of the present invention. Examples of the zwitterion-type ionic liquids include the compound represented by the following Formula 6.

[0049]

[Chem. 6]



(Formula 6)

In the Formula 6, each of R1 and R2 represents an alkyl group. It is synthesized, for example, from a tertiary amine and an alkylsultone (see, for example, Non-Patent Document 6). Although few zwitterion-type ionic liquids are in a liquid state at room temperature, most zwitterion-type ionic liquids are in a liquid state at a temperature of at least 100°C, and thus it is advantageous to use the zwitterion-type ionic liquids for the object of the present invention.

[0050]

The first advantage of adding an ionic liquid in an electrolyte for a capacitor is the anodizing property of the ionic liquid. The second advantage is that the ionic liquid

does not evaporate under normal use conditions due to the excellent stability and the very low vapor pressure of the ionic liquid. In the case where only anodizing property is necessary, the objective is achievable by adding an organic solvent such as ethylene glycol to the conductive polymer. However, this arrangement has a problem that a solvent of this kind will be evaporated off after long time use and therefore the addition effect thereof will be lost. In a conventional liquid electrolyte-type electrolytic capacitor using an organic solvent, a liquid electrolyte that is prepared by adding a solute to the organic solvent is used. However, after evaporation of the organic solvent, the solute added is in a solid state and thus the anodizing property which is the oxide film repairing ability cannot be exerted.

[0051]

As for the electrolyte according to the present invention, it is possible to improve the performance as an electrolyte by adding a solute to the ionic liquid which is a component of the electrolyte. In the electrolyte of the present invention, the added solute is always in a dissolved state in the ionic liquid, and therefore the electrolyte has a higher anodizing ability. It is also possible to control the physical properties, such as lowering of the melting point of the ionic liquid as a component by taking advantage of the freezing point-lowering effect of the added solute.

[0052]

Examples of the additive as an appropriate solute for the aforementioned purposes include ammonium salt additives, such as ammonium adipate; amine salt additives, such as triethylamine maleate; quaternary ammonium salt additives, such as quaternary ammonium maleate and quaternary ammonium phthalate; and quaternary imidazolium salts. Addition of the above additive to the zwitterion-type ionic liquid makes it possible to lower the melting point of the ionic liquid, and thus those additives are advantageous for the object of the

present invention.

[0053]

The conductive polymer as another component of the electrolyte according to the present invention is not particularly limited, but polypyrrole, polythiophene, polyaniline, and derivatives thereof are preferred. An example of the derivatives is a polythiophene derived from a 1,4-dioxythiophene monomer. As a method for synthesizing the conductive polymer, a chemical polymerization method, an electrolytic polymerization method, and an organometallic chemical polycondensation method are used, and the chemical polymerization method and the electrolytic polymerization method are particularly preferably used.

[0054]

The electrolytic polymerization is a method in which, for example, pyrrole monomers are dissolved in a solvent together with a supporting electrolyte and then subjected to dehydrogenation polymerization by anodization. This method is capable of depositing polypyrrole as the conductive polymer on an anode. Since a polymer generally has a lower oxidation-reduction potential than a monomer, oxidation of a polymer skeleton further proceeds in the polymerization process, and anions of the supporting electrolyte are taken as a dopant in the polymer along with the oxidation. This mechanism of the electrolytic polymerization has an advantage that a conductive polymer is obtained without subsequent addition of a dopant.

[0055]

On the other hand, the chemical polymerization is a method in which a raw material monomer, for example, pyrrole, is polymerized by oxidation dehydration in the presence of an appropriate oxidizing agent. As the oxidizing agent, persulfates, hydrogen peroxide, and salts of transition metals such as iron, copper, manganese and the like can be used. Also, as for the conductive polymer synthesized by the chemical polymerization, anions of the oxidizing agent are taken as a

dopant in the polymer during the polymerization process, and thus the conductive polymer can be obtained by one-stage reaction.

[0056]

In the present invention, the dopant of the conductive polymer used as a component of the electrolyte is selected in view of the influence on the conductivity and thermal stability of the conductive polymer. Preferred examples of the dopant used in the present invention include 4-fluoroboric acid ions, p-toluenesulfonic acid ions, anthraquinone-2-sulfonic acid ions, triisopropylnaphthalenesulfonic acid ions, polyvinylsulfonic acid ions, dodecylbenzenesulfonic acid ions, alkylsulfonic acid ions, n-propylphosphoric acid ions, and perchloric acid ions.

[0057]

In order that the dopant is taken in the polymer by the electrolytic polymerization method, the dopant may be dissolved in the form of a sodium salt, an ester, an ammonium salt, or the like, such as sodium p-toluenesulfonate, sodium dodecylbenzenesulfonate, n-propylphosphate, tetra-n-butylammonium perchlorate, or the like, in a solvent such as water, followed by the electrolytic polymerization in the resultant solution.

[0058]

In use as an electrolyte for an electrolytic capacitor, the electrolyte is located on the surface of an oxide film formed on a valve metal such as aluminum, tantalum, or niobium. The metal functions as an anode of the electrolytic capacitor and is used in the form of an etched foil or a sintered compact of a metal powder, for increasing the surface area. Therefore, when the conductive polymer is synthesized by the chemical polymerization, the pores of the etched foil or the spaces of the sintered powder must be filled with the conductive polymer.

[0059]

On the other hand, when the conductive polymer is

synthesized by the electrolytic polymerization, an oxide film on a valve metal is a dielectric, and thus a conductive film must be previously formed on the dielectric for making the dielectric surface conductive, followed by the electrolytic polymerization with the current or voltage applied from a power supply source. As the conductive film to be used for this purpose, a conductive polymer synthesized by the chemical polymerization, pyrolytic manganese dioxide, or the like can be used.

[0060]

Next, description will be made of a method for compounding the ionic liquid and the conductive polymer to form the electrolyte of the present invention. This compounding makes it possible to provide an electrolyte having excellent electron conductivity and excellent anodizing property.

[0061]

The simplest compounding method includes forming the conductive polymer on an oxide film on a valve metal by a known method, immersing the conductive polymer in the ionic liquid, and then pulling up the conductive polymer from the ionic liquid. In forming an electrolytic capacitor, a cathode forming step, an electrode mounting step, an armoring step, and an aging step may be subsequently performed. When an aluminum case is used, for example, for a coiled electrolytic capacitor, the ionic liquid is preferably added into the aluminum case.

[0062]

The amount of the ionic liquid added is selected in a range in which satisfactory anodizing property is exhibited, and the electron conductivity of the conductive polymer is not impaired. From the viewpoint that the electron conductivity is not impaired, generally, the amount of the ionic liquid added is, by weight, preferably 1/2 or less, and more preferably 1/10 or less of that of the conductive polymer. From the viewpoint of the satisfactory anodizing property, the amount of the ionic liquid added is, by weight, preferably 1/1000 or more, and more

preferably 1/100 or more of that of the conductive polymer. In other words, the weight ratio of the ionic liquid to the conductive polymer in the electrolyte of the present invention (i.e., Ionic Liquid/Conductive Polymer) is preferably in a range of from 1/1000 to 1/2 and most preferably from 1/100 to 1/10.

[0063]

A second compounding method uses the ionic liquid as a solvent for synthesizing the conductive polymer by the electrolytic polymerization or chemical polymerization so that the solvent used is positively left, for example, after the step of forming an electrolyte for an electrolytic capacitor. In this case, the weight ratio of the ionic liquid to the conductive polymer (i.e., Ionic Liquid/Conductive Polymer) is, similarly to the above, preferably in a range of from 1/1000 to 1/2 and most preferably from 1/100 to 1/10. In this method, it is more preferable as the compounding method that the anion type of the ionic liquid is the same as that of the dopant of the conductive polymer. By setting the same anion type, electrolytic polymerization and doping of the conductive polymer are simultaneously performed so that an electrolyte having both of excellent electron conductivity and excellent ion conductivity can be provided.

[0064]

As described earlier in the Background Art, there have been cases of studies for synthesizing a conductive polymer by electrolytic polymerization using an ionic liquid as a solvent. In those cases, however, the ionic liquid is used merely as a solvent for the synthesis, and the polymerized conductive polymer and the ionic liquid as a polymerization solvent are separated. Alternatively, unlike the electrolyte of the present invention, they are not present at least in the required proportions for an electrolyte having both of excellent electron conductivity and excellent ion conductivity. Moreover, in those cases, the ionic liquid used as a

polymerization solvent contains a halogen. Since an electrolyte is generally used for electronics devices, the substance containing a halogen which tends to corrode a metal is not appropriate as an electrolyte. Furthermore, no case has been known where the ionic liquid is used as a solvent for synthesizing the conductive polymer by chemical polymerization, and the ionic liquid is positively left after the polymerization, or is added to the polymerized conductive polymer.

[0065]

[Examples]

(Synthesis of Ionic Liquid)

First, synthesis examples of the ionic liquid used as a component of the electrolyte of the present invention is described.

(1) N-Ethylimidazolium acetate (hereinafter abbreviated as ILS-1)

[0066]

6 ml of 99.7% acetic acid was added to 10 g of N-ethylimidazole, and the resultant mixture was stirred for 12 hours at a temperature kept at 0°C. The resultant reaction product was added dropwise to 1000 ml of diethyl ether under stirring. The diethyl ether was distilled off at room temperature, and the residue was dried under vacuum to yield crystals. The crystals were collected to obtain 15.9 g of N-ethylimidazolium acetate. The product had a glass transition temperature of -51.7°C.

(2) 1-(N-Ethylimidazolio)butane-4-sulfonate (hereinafter abbreviated as ILS-2)

[0067]

First, 5.30 g (55.1 mmol) of N-ethylimidazole was dissolved in 50 ml of acetone. Next, 7.61 g (55.9 ml) of propane sultone was dissolved in 100 ml of acetone, and the resultant solution was added dropwise to the acetone solution of N-ethylimidazole at room temperature, followed by stirring for 91 hours at room temperature for reaction. The resultant

reaction mixture was filtered by suction using a Nutsche provided with a glass filter. The product filtered off on the glass filter was sufficiently washed with excess acetone and then dried under vacuum to obtain 1.42 g of the product. The yield was 11.1%. The product was identified as an imidazolium salt (Formula 7) by its ^{1}H-NMR spectrum. As a result of measurement by differential scanning calorimetry (DSC), the melting point was -10°C.

[0068]

[Chem. 7]

(Formula 7)

[Spectral data]: 500 MHz, ^{1}H-NMR (DMSO-d_6) σ=1.36 (triplet, 3H), 1.48 (triplet, 2H), 1.84 (triplet, 2H), 2.36 (triplet, 2H), 4.13 (multiplet, 4H), 7.77 (d.d., 2H), 9.20 (singlet, 1H)

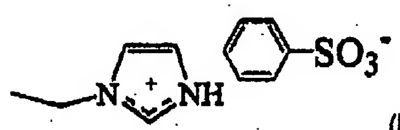
(3) 3-Ethyl-imidazolium benzenesulfonate (hereinafter abbreviated as ILS-3)

[0069]

First, 3.12 g (32.4 mmol) of N-ethylimidazole was dissolved in 50 ml of ethanol. Next, 5.72 g (32.4 mmol) of benzenesulfonic acid monohydrate was rapidly added to the N-ethylimidazole ethanol solution under ice-cooling, followed by stirring for 23 hours. The ethanol was distilled off with an evaporator, and the residual reaction solution was added dropwise to 200 ml of ether cooled with dry ice. The resultant mixture was rapidly filtered by suction using a Nutsche provided with a glass filter to collect 8.10 g of a white solid on the glass filter. The yield was 91.6%. The product was identified as an imidazolium salt (Formula 8) by its ^{1}H-NMR spectrum. The obtained imidazolium salt had a glass transition temperature (Tg) of 4.3°C.

[0070]

[Chem. 8]



(Formula 8)

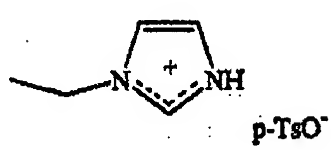
[Spectral data]: 500 MHz, ^{1}H-NMR (DMSO-d_6, σ) σ=1.34 (triplet, J=5Hz, 3H), 4.15 (quarlet, J=5 Hz, 2H), 7.26 (multiplet, 3H), 7.58 (multiplet, 3H), 7.73 (singlet, 1H), 9.04 (singlet, 1H)

(4) 3-Ethyl-imidazolium p-toluenesulfonate (hereinafter abbreviated as ILS-4)

First, 4.02 g (41.7 mmol) of N-ethylimidazole was dissolved in 50 ml of ethanol. Next, 8.35 g (41.7 mmol) of p-toluenesulfonic acid monohydrate was rapidly added to the N-ethylimidazole ethanol solution under ice-cooling, followed by stirring for 23 hours. The ethanol was distilled off with an evaporator, and the residual reaction solution was added dropwise to 200 ml of ether cooled with dry ice. The resultant mixture was rapidly filtered by suction using a Nutsche provided with a glass filter to collect 8.10 g of the product on the glass filter. The yield was 65.5%. The product was identified as an imidazolium salt (Formula 9) by its ^{1}H-NMR spectrum. The obtained imidazolium salt had a glass transition temperature (Tg) of 4.3°C.

[0071]

[Chem. 9]



(Formula 9)

[Spectral data]: 500 MHz, ^{1}H-NMR (DMSO-d_6, σ) σ=1.35 (triplet, J=5 Hz, 3H), 2.23 (singlet, 3H), 4.15 (quarlet, J=5 Hz, 2H), 7.06 (doublet, J=5 Hz, 2H), 7.44 (doublet, J=5 Hz, 2H), 7.74 (singlet, 2H), 9.04 (singlet, 1H)

(5) 1-Butyl-imidazolium p-toluenesulfonate (hereinafter abbreviated as ILS-5)

[0072]

First, 3.80 g (30.6 mmol) of N-butylimidazole was dissolved in 20 ml of DMF (dimethylformamide). Next, 5.20 g (30.6 mmol) of p-toluenesulfonic acid monohydrate was rapidly added to the N-butylimidazole DMF solution under ice-cooling, followed by stirring for 23 hours. The reaction solution was added dropwise to 200 ml of ether cooled with dry ice. The resultant mixture was filtered by suction using a Nutsche provided with a glass filter to collect 6.40 g of a white solid on the glass filter. The yield was 70.6%. The collected product was identified as an imidazolium salt (Formula 10) by its ^{1}H-NMR spectrum. The obtained imidazolium salt had a glass transition temperature (Tg) of -38.4°C and a crystallization temperature (Tc) of 2.6°C.

[0073]

[Chem. 10]

(Formula 10)

[Spectral data]: 500 MHz, ^{1}H-NMR (DMSO-d_6) σ=0.84 (triplet, J=5 Hz, 3H), 1.16 (multiplet, 2H), 1.71 (multiplet, 2H), 2.23 (singlet, 3H), 4.11 (triplet, J=5 Hz, 2H), 7.07 (doublet, J=5 Hz, 2H), 7.44 (doublet, J=5 Hz, 2H), 7.60 (singlet, 1H), 7.71 (singlet, 1H), 9.04 (singlet, 3H)

(6) 1-Ethyl-3-ethylimidazolium p-toluenesulfonate (hereinafter abbreviated as ILS-6)

[0074]

In a dry 200-ml round-bottom flask, 4.02 g (41.7 mmol) of N-ethylimidazole and 20 ml of DMF were charged, and the resultant mixture was sufficiently stirred. Then, 8.35 g (41.7 mmol) of ethyl p-toluenesulfonate was rapidly added to the flask

under ice-cooling. After the addition, the mixture was further stirred for 23 hours. The reaction solution was added dropwise to 200 ml of ice-cooled ether. The ether was decanted to obtain 8.1 g of a yellow liquid. The yield was 65.5%. The obtained liquid was identified as an imidazolium salt (Formula 11) by its ^{1}H-NMR spectrum. The obtained imidazolium salt had a glass transition temperature (Tg) of −59.5°C.

[0075]

[Chem. 11]

(Formula 11)

[Spectral data]: 500 MHz, ^{1}H-NMR (DMSO-d_6) σ=1.35 (triplet, J=5 Hz, 3H), 2.23 (singlet, 3H), 4.15 (quarlet, J=5 Hz, 2H), 7.06 (doublet, J=5 Hz, 2H), 7.44 (doublet, J=5 Hz, 2H), 7.74 (singlet, 2H), 9.04 (singlet, 3H)

(7) 1-Methyl-3-ethylimidazolium p-toluenesulfonate (hereinafter abbreviated as ILS-7)

In a dry 200-ml round-bottom flask, 2.30 g (28.0 mmol) of N-methylimidazole and 20 ml of DMF were charged, and the resultant mixture was sufficiently stirred. Then, 5.61 g (28.0 mmol) of ethyl p-toluenesulfonate was rapidly added to the flask under ice-cooling. After the addition, the mixture was further stirred for 23 hours. The reaction solution was added dropwise to 200 ml of ice-cooled ether. The ether was decanted to obtain 5.90 g of a yellow liquid. The yield was 74.4%. The obtained liquid was identified as an imidazolium salt (Formula 12) by its ^{1}H-NMR spectrum. The obtained imidazolium salt had a glass transition temperature (Tg) of −85.7°C.

[0076]

[Chem. 12]

p-TsO⁻ (Formula 12)

[Spectral data]: 500 MHz, ^{1}H-NMR (DMSO-d_6) σ=1.33(triplet, J=5 Hz, 3H), 2.22 (singlet, 3H), 3.77 (singlet, 3H), 4.12 (quarlet, J=5 Hz, 2H), 7.06 (doublet, J=5 Hz, 2H), 7.44 (doublet, J=5 Hz, 2H), 7.65 (singlet, 2H), 7.72 (singlet, 2H), 9.08 (singlet, 3H)

(8) 1-Butyl-3-ethylimidazolium p-toluenesulfonate (hereinafter abbreviated as ILS-8)

[0077]

First, 0.60 g (4.83 mmol) of N-butylimidazole was dissolved in 20 ml of DMF, and to the solution was rapidly added 0.97 g (4.83 mmol) of ethyl p-toluenesulfonate under ice-cooling. After the addition, the mixture was further stirred for 23 hours. The reaction solution was added dropwise to 200 ml of ice-cooled ether. The ether was decanted to obtain 0.36 g of a yellow liquid. The yield was 0.26%. The obtained liquid was identified as an imidazolium salt (Formula 13) by its ^{1}H-NMR spectrum. The obtained imidazolium salt had a glass transition temperature (Tg) of -73.8°C.

[0078]

[Chem. 13]

p-TsO⁻ (Formula 13)

[Spectral data]: 500 MHz, ^{1}H-NMR (DMSO-d_6) σ=0.84 (triplet, J=5 Hz, 3H), 1.16 (multiplet, 2H), 1.33 (triplet, J=5 Hz, 3H), 2.22 (singlet, 3H), 4.12 (quarlet, J=5 Hz, 2H), 7.07 (doublet, J=5 Hz, 2H), 7.44 (doublet, J=5 Hz, 2H), 7.60 (singlet, 1H), 7.71 (singlet, 1H), 9.04 (singlet, 1H)

(9) N-Vinylimidazolium methanesulfonate (hereinafter abbreviated as ILS-9)

First, 7 ml of methanesulfonic acid was added to 10 g of N-vinylimidazole, and the resultant mixture was stirred for 3 hours at a temperature kept at 0°C and then added dropwise to diethyl ether cooled with dry ice. The resultant mixture was rapidly filtered by suction using a Nutsche provided with a glass filter to collect crystals on the glass filter. The crystals were dried to obtain 19.2 g of N-vinylimidazolium methanesulfonate. The yield was 95%, and the melting point was 5°C.

(10) N-Vinylimidazolium Molten Salt Polymer (hereinafter abbreviated as ILS-10)

[0079]

First, 1.0 g of the ILS-9 was dissolved in 10 ml of methanol, and to the resultant solution was added azobisisobutyronitrile as a polymerization initiator at 1% by mole relative to vinyl units of the ILS-9. Then, radical polymerization was performed at a temperature of 65°C for 3 hours to obtain N-vinylimidazolium molten salt polymer (ILS-10).

[0080]

(Examples 1 to 10)

An electrolytic capacitor was experimentally produced using a conductive polymer formed on an aluminum oxide film by electrolytic polymerization. Each of the ionic liquids obtained above was added to the produced electrolytic capacitor, and then the capacitor properties were measured.

[0081]

Specifically, an aluminum foil (etched aluminum foil) of 7 mm in length and 10 mm in width was immersed in a 3% aqueous solution of ammonium adipate, the aluminum foil being provided with an anode lead and having pores formed in the surface by etching. Then, anodization was performed at 70°C with a voltage of 70 V applied to form an oxide film as a dielectric film on the surface of the aluminum foil. Next, the resultant aluminum foil was immersed in a 30% aqueous solution of manganese nitrate, naturally dried, and then subjected to pyrolysis at 300°C for

30 minutes to form a conductive layer including a manganese oxide layer on the dielectric film.

[0082]

Next, a polypyrrole layer was formed on the foil by electrolytic polymerization. FIG. 1 is a conceptual diagram of the apparatus used. An electrolytic solution (6) used for polymerization contains pyrrole (0.5 M (mol/l)), a 30% alcohol solution of sodium triisopropylnaphthalenesulfonate (0.1 M), and water. As shown in FIG. 1, an aluminum foil (2) was disposed in an electrolytic polymerization solution, and a polymerization initiation electrode (1) was brought near to a manganese dioxide conductive layer (4). Then, a constant voltage of 1.5 V was applied across the polymerization initiation electrode (1) and a cathode (7) for 50 minutes to perform electrolytic polymerization reaction. As a result, an electrolytically polymerized polypyrrole layer (5) was formed on the conductive layer.

[0083]

Then, the aluminum foil having the polypyrrole layer was washed with water, dried, immersed in a methanol solution of an ionic liquid, and then dried to remove methanol. By such a method, each ionic liquid was added to the electrolytically polymerized polypyrrole layer to obtain an electrolyte of the present invention. The amount of the ionic liquid added was 0.5 to 5% by weight of the conductive polymer. Next, a carbon layer and a silver paste layer were provided on the electrolyte of the present invention to prepare a capacitor. The resultant capacitor of the present invention was aged at 20 V for 1 hour, and then the initial capacitance, tan δ, impedance (120 Hz), and withstand voltage (V) were measured.

[0084]

Table 1 shows the properties of the resultant capacitors. The initial capacitance, tan δ, and impedance of Examples were not so different from those of Comparative Example in which the ionic liquid was not added, but the withstand voltage of

Examples was significantly improved. It was thus found that improvement in the withstand voltage of an electrolytic capacitor could be realized by applying the electrolyte of the present invention to the electrolytic capacitor, the electrolyte being prepared by adding an ionic liquid to a conductive polymer.

[0085]

[Table 1]

Example Nos.	Added ionic liquids	Initial Properties			
		Capacitance (μF)	Tan δ (%)	Impedance (mΩ)	Withstand voltage (V)
Example 1	ILS-1	4.8	1.1	92	25
Example 2	ILS-2	4.7	1.2	95	28
Example 3	ILS-3	4.6	1.2	92	25
Example 4	ILS-4	4.8	1.1	88	25
Example 5	ILS-5	4.7	1.1	90	24
Example 6	ILS-6	4.6	1.2	95	28
Example 7	ILS-7	4.5	1.2	95	27
Example 8	ILS-8	4.8	1.2	90	26
Example 9	ILS-9	4.8	1.2	92	24
Example 10	ILS-10	4.6	1.1	98	28
Comparative Example 1	-	4.8	1.1	90	16

(Examples 11 to 20)

A conductive polymer electrolytic capacitor was produced using a conductive polymer formed on a tantalum oxide film by chemical polymerization. Each of the ionic liquids obtained above was added to the produced electrolytic capacitor, and then the capacitor properties were measured.

[0086]

Specifically, a rectangular parallelepiped tantalum sintered compact (2 mm in length, 1.5 mm in height, and 1 mm in width) provided with an anode lead was subjected to anodization at 85°C for 60 minutes with a voltage of 33.9 V applied in a 0.05% aqueous phosphoric acid solution to form an

oxide film as a dielectric film on the tantalum sintered compact, thereby preparing a sample.

[0087]

The sample was immersed in a 0.75 mol/l aqueous solution of pyrrole for 2 minutes and then immersed in a 0.1 mol/l aqueous ferric sulfate solution for 10 minutes. This operation was repeated about 20 times to cover the entire surface of the sample with polypyrrole by chemical polymerization. Then, the sample was washed with water, dried, immersed in a methanol solution of an ionic liquid, and then dried to remove methanol. By such a method, each ionic liquid was added to the chemically polymerized polypyrrole layer to obtain an electrolyte of the present invention. The amount of the ionic liquid added was 0.5 to 5% by weight of the conductive polymer.

[0088]

Next, a carbon layer and a silver paste layer were provided on the electrolyte of the present invention to prepare a capacitor. A cathode lead was provided on the silver paste layer, and the resultant product was aged at an applied voltage of 12.5 V for 1 hour, and then armored with a resin to obtain an electrolytic capacitor. The thus-prepared capacitor of the present invention was aged at 20 V for 1 hour. Then, the initial capacitance, tan δ, leakage current, and withstand voltage (V) were measured.

[0089]

Table 2 shows the properties of the resultant capacitors. The initial capacitance and tan δ of Examples were not so different from those of Comparative Example in which the ionic liquid was not added, but the leakage current and withstand voltage of Examples were significantly improved. It was thus found that improvement in the withstand voltage of an electrolytic capacitor could be realized by applying the electrolyte of the present invention to the electrolytic capacitor, the electrolyte being prepared by adding an ionic liquid to a conductive polymer.

[0090]

[Table 2]

Example Nos.	Added ionic liquide	Initial Properties			
		Capacitance (μF)	Tan δ (%)	Leakage current (μA)	Withstand voltage (V)
Example 11	ILS-1	16.6	1.7	0.10	16
Example 12	ILS-2	16.9	1.8	0.12	16
Example 13	ILS-3	17.7	2.0	0.08	16
Example 14	ILS-4	16.8	1.8	0.09	16
Example 15	ILS-5	17.5	1.7	0.12	16
Example 16	ILS-6	16.7	1.6	0.13	18
Example 17	ILS-7	16.2	1.7	0.16	16
Example 18	ILS-8	17.0	1.8	0.12	18
Example 19	ILS-9	17.0	1.8	0.08	20
Example 20	ILS-10	16.5	2.0	0.13	20
Comparative Example 2	-	17.2	1.8	0.18	12

(Examples 21 to 30)

A conductive polymer aluminum electrolytic capacitor was prepared using a conductive polymer formed on an aluminum oxide film by the chemical polymerization of thiophene.

[0091]

Specifically, an etched aluminum foil of 4×3.3 mm was immersed in a 3% aqueous solution of ammonium adipate. Next, the applied voltage was increased from 0 V to 10 V at a rate of 10 mV/sec, and a constant voltage of 10 V was subsequently applied for 40 minutes to form a dielectric film on the etched aluminum foil. Next, the foil was washed with flowing deionized water for 10 minutes and then dried at 105°C for 5 minutes. The capacitance of the resultant etched aluminum foil in the solution was 18 μF.

[0092]

Next, an ethanol solution containing ferric benzenesulfonate which was a transition metal salt including a benzenesulfonic acid anion and ferric

triisopropylnaphthalenesulfonate which was a transition metal salt including a triisopropylnaphthalenesulfonic acid anion was prepared as an oxidizing agent. Next, 1,4-dioxythiophene was mixed with the oxidizing agent, and the resultant mixture was stirred to prepare a polymerization solution. The aluminum foil anodized as described above was immersed in the solution, heated in an electric furnace at 105°C for 5 seconds, further heated in an electric furnace at 70°C for 10 minutes to progress chemical polymerization, washed with deionized water, and then dried. This operation was repeated ten or more times so that the foil was entirely covered with polythiophene as viewed with the eyes. After washing and drying, each of the ionic liquids was added by the same method as in Examples 1 to 10. Then, a carbon layer and a silver paste layer were provided on the obtained electrolyte to prepare a capacitor.

[0093]

The properties of the resultant capacitors are shown in Table 3. The initial capacitance and tan δ of Examples were not so different from those of Comparative Example in which the ionic liquid was not added, but the leakage current and withstand voltage of Examples were significantly improved. It was thus found that improvement in the properties of an electrolytic capacitor could be realized by applying the electrolyte of the present invention to the electrolytic capacitor, the electrolyte being prepared by adding an ionic liquid to a conductive polymer.

[0094]

[Table 3]

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Example Nos.	Added ionic liquids	Initial Properties			
		Capacitance (μF)	Tan δ (%)	Leakage current (μA)	Withstand voltage (V)
Example 21	ILS-1	15.2	1.9	0.08	8
Example 22	ILS-2	15.9	2.1	0.14	8
Example 23	ILS-3	15.0	2.0	0.04	8
Example 24	ILS-4	15.0	2.2	0.09	6
Example 25	ILS-5	15.5	2.2	0.11	8
Example 26	ILS-6	15.0	2.1	0.03	6
Example 27	ILS-7	16.1	1.8	0.06	8
Example 28	ILS-8	15.0	2.4	0.10	8
Example 29	ILS-9	15.0	2.8	0.08	8
Example 30	ILS-10	14.9	2.6	0.10	9
Comparative Example 3	-	15.2	2.0	0.28	4

(Examples 31 to 35)

A methanol solution containing the ionic liquid (ILS-7) and each of the following solutes (for the ionic liquid): ammonium adipate (IL-A) in Example 31; triethylamine maleate (IL-B) in Example 32; tetraethylammonium maleate (IL-C) in Example 33; tetraethylammonium phthalate (IL-D) in Example 34; and tetraethylammonium benzoate (IL-E) in Example 35, at a weight ratio of 2:1 was prepared. Thereafter, a capacitor was produced in the same manner as in Example 7. Namely, instead of the step of immersing in the ILS-7 methanol solution in Example 7, the step of immersing in a methanol solution of ILS-7 containing each solute was performed.

[0095]

The properties of the resultant capacitors are shown in Table 4. As shown in Table 4, when the electrolyte of the present invention prepared by adding an ionic liquid containing such a solute to a conductive polymer was applied to an electrolytic capacitor, the withstand voltage of the capacitor could be further improved.

[0096]

[Table 4]

Example Nos.	Added ionic liquids	Initial Properties			
		Capacitance (μF)	Tan δ (%)	Impedance (mΩ)	Withstand voltage (V)
Example 31	IL-A	4.5	1.2	94	32
Example 32	IL-B	4.4	1.2	98	34
Example 33	IL-C	4.5	1.2	94	30
Example 34	IL-D	4.3	1.2	98	30
Example 35	IL-E	4.6	1.3	94	32

[0097]

[Effect of the Invention]

The electrolyte of the present invention contains at least both a conductive polymer and an ionic liquid. This constitution allows the electrolyte of the present invention to achieve excellent electron conductivity and excellent ion conductivity. Use of the electrolyte for an electrolyte of an electrolytic capacitor can provide an electrolytic capacitor having excellent high-frequency properties and a high withstand voltage.

[Brief Description of the Drawings]

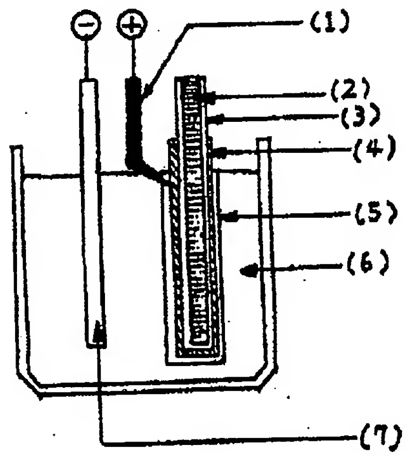
[Fig. 1] Fig. 1 is a conceptual diagram of an electrolytic polymerization apparatus for a conductive polymer.

[Reference Numerals]

1 polymerization initiation electrode
2 aluminum foil
3 dielectric layer
4 manganese dioxide conductive layer
5 conductive polymer layer
6 electrolytic solution
7 cathode

[Document Name] Drawings

[Fig.1]



JP-A 2003-204299

[Document Name] Abstract

[Abstract]

[Subject] To provide a capacitor having high withstand voltage without losing excellent high-frequency properties of a conductive polymer capacitor.

[Constitution] The subject is achieved by (1) using an electrolyte which contains an ionic liquid and a conductive polymer as essential ingredients; (2) using a halogen-free ionic liquid for the ionic liquid; (3) using the ionic liquid in which an anionic component contains a carboxylate ion ($-COO^-$) or a sulfonic acid anion ($-SO_3^-$); (4) adding at least one salt selected from ammonium salts, amine salts, quaternary ammonium salts, and organic acids to the ionic liquid.

[Selective Figure] None